

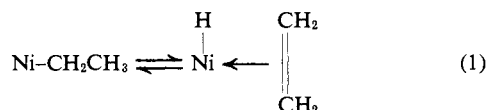
Structure of (2,4-Pentanedionato)(triphenylphosphine)ethylnickel(II) in the Crystalline State and in Solution

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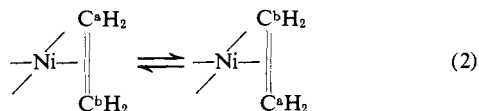
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Abstract: The structural nature of the title compound has been thoroughly investigated following a report that all ethyl protons are nmr equivalent and the suggestion that this might be attributed to scrambling *via* a rapid, reversible tautomerization of the ethylnickel moiety to an ethylenickel hydrido moiety. A single-crystal X-ray structural study demonstrates that the compound does have the anticipated ethylnickel moiety in a normal stereochemical configuration. The set of four ligand atoms about the nickel atom is essentially planar and the 2,4-pentanedionato ligand is planar and symmetrical. The following dimensions of the ethylnickel moiety were found: Ni-C, 1.97 (1), C-C, 1.56 (1) Å; \angle Ni-C-C, 108.1 (9)°. In benzene solution the proton nmr spectrum is, as reported, entirely consistent with such a structure except that all five ethyl hydrogen atoms give rise to a sharp (2 Hz) singlet of the correct integrated intensity. However, the ^{13}C spectrum (natural abundance level) shows that this is due to accidental equality of proton chemical shifts and not to scrambling, since a normal ^{13}C spectrum for the ethyl group is observed. Occurrence of the postulated tautomerism would have to be followed by rotation of the ethylene ligand in order for scrambling to occur. Evidently, one or both of these steps is too slow or fails to occur at all. Crystal data: space group $P\bar{1}$; $a = 9.297$ (2), $b = 11.026$ (7), $c = 13.188$ (6) Å; $\alpha = 106.05$ (4), $\beta = 110.37$ (3), $\gamma = 101.38$ (4)°; $V = 1151.5$ (9) Å³; $Z = 2$.

Compounds of the type $\text{Ni}(\text{acac})(\text{PR}_3)\text{R}'$ have only recently been described.^{1,2} More recently, Yamamoto and coworkers reported the new compound, **1**, in which $\text{R} = \text{C}_6\text{H}_5$ and $\text{R}' = \text{C}_2\text{H}_5$, including a novel observation concerning its proton nmr spectrum in nonpolar solvents.³ They found that the ethyl group was represented by only a single sharp line in the spectrum recorded on solutions in benzene and acetone although a more complex signal consistent with separate but overlapping resonances for the methylene and methyl protons was observed in pyridine. To explain this they suggested the possibility that the methylene and methyl protons were being scrambled rapidly on the nmr time scale by the following process



It is important to recognize that the above process would not in itself lead to scrambling of the hydrogen atoms. It is also necessary that the ethylene ligand undergo rapid rotation about the axis from the nickel atom to the center of the C-C bond, *e.g.*, (2). Such



rotations are known to occur in both planar and octahedral olefin complexes in a number of cases,⁴⁻⁷ but it

(1) P. W. Jolly, K. Jonas, C. Kruger, and Y.-H. Tsay, *J. Organometal. Chem.*, **33**, 109 (1971).

(2) B. L. Barnett and C. Kruger, *J. Organometal. Chem.*, **42**, 169 (1972).

(3) A. Yamamoto, T. Yamamoto, T. Saruyama, and Y. Nakamura, *J. Amer. Chem. Soc.*, **95**, 4073 (1973).

(4) R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964).

(5) J. Ashley-Smith, I. Douek, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1776 (1972).

(6) B. F. G. Johnson and J. A. Segal, *J. Chem. Soc., Chem. Commun.*, 1312 (1972).

(7) M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **12**, 991 (1973)

cannot be assumed that rotation would necessarily be rapid in the present case.

The findings, of Yamamoto, *et al.*, and their speculations thereon, seemed to us to be of unusual interest since, if valid, this and related systems would afford an opportunity to make direct nmr observations of the reversible process of β -hydrogen to metal shifts and of its dependence on solvent, temperature, and other ligands in the complex. This process is already known to be of fundamental importance in various phases of transition metal organometallic chemistry,⁸ but considerably more detailed information on it would be welcome and useful.

Consequently, we contemplated a program of investigation of **1** and its homologs, beginning with two specific studies: (1) a crystallographic study of **1** to determine if its structure is in fact that assumed, (2) a further study of its behavior in solution to determine whether the proposed scrambling of ethyl hydrogen atoms really occurs and, if so, to ascertain the rate and activation parameters of the process. The first concern under point 2 was to employ ^{13}C nmr to verify the occurrence of the process represented in eq 1 and 2. If the complete and rapid scrambling of the ethyl hydrogen atoms is occurring *via* processes 1 and 2, the ^{13}C nmr signal for the ethyl carbon atoms should be a 1:5:10:10:5:1 sextet when observed without broad-band proton decoupling and, of course, a singlet with decoupling.

Experimental Section

All preparations were carried out in an atmosphere of nitrogen. Solvents were dried over sodium benzophenone and distilled under nitrogen just prior to use. Nickel acetylacetonate was purchased from Alfa Inorganics, Beverly, Mass., and dehydrated by maintaining a temperature of 100° while under vacuum for 24 hr. Triphenylphosphine and triethylaluminum were purchased from

(8) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley-Interscience, 1972, pp 756-761, 785-792.

Table II. Positional and Thermal Parameters and Their Standard Deviations for Anisotropically Refined Atoms^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	-0.1037 (2)	-0.2225 (2)	0.1939 (1)	0.0115 (3)	0.0099 (2)	0.0061 (2)	0.0046 (2)	0.0029 (2)	0.0025 (1)
P	-0.0510 (4)	-0.3287 (3)	0.3081 (3)	0.0120 (6)	0.0100 (5)	0.0063 (3)	0.0046 (4)	0.0037 (4)	0.0026 (3)
O(1)	-0.330 (1)	-0.2860 (9)	0.1543 (8)	0.014 (2)	0.018 (1)	0.0084 (9)	0.006 (1)	0.003 (1)	0.007 (1)
O(2)	-0.136 (1)	-0.1282 (9)	0.0903 (7)	0.015 (2)	0.013 (1)	0.0081 (9)	0.006 (1)	0.003 (1)	0.0053 (9)
C(1)	0.130 (1)	-0.155 (1)	0.235 (1)	0.008 (2)	0.014 (2)	0.011 (1)	0.004 (2)	0.005 (1)	0.005 (1)
C(2)	0.190 (2)	-0.000 (1)	0.298 (1)	0.019 (3)	0.010 (2)	0.012 (2)	-0.001 (2)	0.005 (2)	0.002 (1)
C(3)	-0.443 (2)	-0.260 (1)	0.084 (1)	0.013 (2)	0.016 (2)	0.006 (1)	0.008 (2)	0.001 (1)	0.002 (1)
C(4)	-0.274 (2)	-0.121 (1)	0.027 (1)	0.015 (3)	0.012 (2)	0.007 (1)	0.006 (2)	0.003 (2)	0.002 (1)
C(5)	-0.615 (2)	-0.328 (2)	0.071 (1)	0.011 (3)	0.023 (3)	0.017 (2)	0.005 (2)	0.005 (2)	0.009 (2)
C(6)	-0.261 (2)	-0.035 (1)	-0.045 (2)	0.026 (3)	0.013 (2)	0.013 (2)	0.006 (2)	0.005 (2)	0.009 (2)
C(7)	-0.425 (2)	-0.184 (1)	0.021 (1)	0.015 (3)	0.011 (2)	0.009 (2)	0.006 (2)	0.004 (2)	0.005 (1)

^a Numbers in parentheses are estimated standard deviations in the last significant digit.

Orgmet, Inc., E. Hampstead, N. H., and used without further purification.

Preparation. A solution of diethylaluminum monoethoxide prepared in 30 ml of hexane from 1.5 ml (20 mmol) of triethylaluminum and 5.25 ml (20 mmol) of absolute ethanol was added dropwise to a stirred mixture of 5.0 g (20 mmol) of nickel acetylacetonate and 5.25 g (20 mmol) of triphenylphosphine in 75 ml of ether⁹ cooled to -20° . The temperature⁹ was allowed to rise slowly to 10° and was maintained there for 45 min. The mixture was filtered to remove unreacted material, which was washed with 30 ml of hexane. The filtrate was then placed in the freezer (ca. 0°) overnight. The solvent was removed, and the reddish yellow crystals were washed with hexane (three 10-ml portions), yield 5.5 g (63% theory). It melts, $94-99^\circ$, with decomposition to a light green product. It is stable in air for several hours but decomposes rapidly in chloroform. The infrared spectrum in ether is blank in the region from 2100 to 1700 cm^{-1} where an absorption for Ni-H is expected.

Spectroscopic Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 451 spectrophotometer and calibrated with polystyrene. Pmr spectra were recorded on a Varian Associates HA-100 spectrometer. Temperature calibrations for the variable temperature spectra were obtained from either methanol or ethylene glycol standards and are expected to be accurate to $\pm 3^\circ$. Carbon-13 nmr spectra were recorded on a JEOL-JNM-PS-100/Nicolet 1080 Fourier transform spectrometer. The spectra in Figure 5 were obtained with these experimental parameters. With the spectrometer at 24.9186 MHz and a width of 5 μsec (tilt angle equals 90° when the width is 17 μsec), 512 sweeps in toluene- d_6 were collected to obtain the decoupled spectrum. Changing the spectrometer frequency to 24.9117 MHz and the width to 7 μsec and filtering only 2000 of the 6850 Hz sweep width to decrease the contribution of the aromatic carbons to the FID, 32,768 sweeps in benzene- d_6 were recorded to give the coupled spectrum. Samples were prepared in an inert atmosphere in serum stopper-adapted nmr tubes. Solvents were vacuum degassed and admitted to the samples from a syringe.

Collection of X-Ray Data. A yellow, well-formed crystal, grown during the sample preparation, was used. The crystal of approximate dimensions $0.20 \times 0.20 \times 0.10\text{ mm}$ was fixed in a glass capillary with epoxy glue. Data were collected at a temperature of $18 \pm 2^\circ$ on a Syntex PI automated diffractometer using Mo $K\alpha$ radiation monochromatized with a graphite crystal in the incident beam. The unit cell was found to be triclinic, and least-squares refinement of 15 centered reflections produced the orientation matrix for data collection and gave the following unit cell dimensions: $a = 9.297 (2)$, $b = 11.026 (7)$, $c = 13.188 (6)\text{ \AA}$; $\alpha = 106.05 (4)$, $\beta = 110.37 (3)$, $\gamma = 101.38 (4)^\circ$; $V = 1151.5 (9)\text{ \AA}^3$. The space group is $P\bar{1}$. Assuming the cell contains two formula units of $\text{NiC}_{23}\text{H}_{27}\text{O}_2\text{P}$, formula weight 449.2, the calculated density is 1.30 g cm^{-3} .

Intensity data were collected in the range $0^\circ < 2\theta \leq 47.5^\circ$. The $\theta-2\theta$ scan technique with a variable scan rate from 3 to $24^\circ/\text{min}$ and a scan range from $2\theta(\text{Mo } K\alpha_1) - 0.7^\circ$ to $2\theta(\text{Mo } K\alpha_2) + 0.7^\circ$ was

used. The intensities of three standard reflections, measured every 100 reflections, showed no significant variation.

The intensities of 3115 independent reflections were recorded in this way, of which 1437 had intensities three times greater than their estimated standard deviations, $\sigma(I)$, after Lorentz and polarization corrections were applied to the data. Here $\sigma(I)$ is calculated from the expression given previously¹⁰ using values of 0.065 and 0.5 for p and R , respectively. No absorption correction ($\mu = 9.31\text{ cm}^{-1}$) was made.

Structure Solution and Refinement.¹¹ The structure determination was first approached using conventional Patterson techniques, but a solution for the Ni and P atoms which lead to a complete structure was not found. Consequently, recourse was had to direct methods, as embodied in the MULTAN program.¹¹ The original Patterson solution was found to be incorrect; the new Ni and P positions were refined to give

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum F_o} = 0.320$$

and

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.397$$

(not significantly different from those reached with the previous, incorrect solution), and a difference electron density map was then calculated. This afforded positions for the oxygen atoms and for those carbon atoms subsequently numbered 1, 3, 4, 11, 14, 22, 26, 31, 32, and 36. This much of the structure was then refined to R_1 and R_2 values of 0.25 and 0.32, respectively.

In all refinements the atomic scattering factors were taken from the tabulation of Cromer and Waber¹² and corrected for anomalous dispersion using $\Delta f'$ and $\Delta f''$ values from Cromer and Liberman.¹³

All the remaining non-hydrogen atoms were found on the next difference map, and two cycles of isotropic refinement converged to R values of 0.084 and 0.097. Three more cycles in which the phenyl carbon atoms were still refined isotropically but all other atoms were given anisotropic temperature parameters converged to R values of 0.068 and 0.082. Refinement was terminated at this point since the structure was sufficiently complete and accurate to answer all questions relevant to this investigation.

A final difference map had no peak with a density in excess of 0.45 e\AA^{-3} while the density of a carbon was about 2.5 e\AA^{-3} . Shifts in the last cycle of least-squares refinement were all less than 0.12

(10) F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organometal. Chem.*, **50**, 227 (1973).

(11) The following computer programs written for the IBM 360 were used: DATARED, a data reduction program by Frenz; MULTAN, a direct methods program based on a version by Main, Woolfson, and Germain; FOURIER, a Fourier summation program (based on Zalkin's FORDAP) by Dellaca and Robinson; NUCLS, a least-squares program by Ibers and Doedens which closely resembles Busing and Levy's ORFLS program, the quantity minimized is $\sum w(|F_o| - |F_c|)^2$; SADIAN, a program for calculating atomic distances and angles by Baur; PERFECT, a program for analysis of structure factors by Frenz; ORTEP, a plotting program by Johnson; ORFFE, a function and error program by Busing, Martin, and Levy and modified by Brown, Johnson, and Thiessen; and LIST, a data listing program by Snyder.

(12) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, in preparation.

(13) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(9) In our hands, the use of toluene solvent at -30° for 40 hr, as briefly described by Yamamoto,³ did not afford an isolable product, although it was tried several times. Reaction occurred and the color of the solution indicated that the product had formed, but it could not be isolated. Hence, our procedure differs, particularly in the use of ether as a solvent.

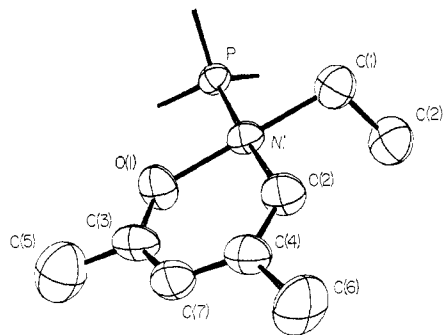


Figure 1. A view of the molecular structure excluding the phenyl rings for clarity. The atom numbering scheme defined is followed in the tables. Atoms are represented by thermal vibration ellipsoids enclosing 50% of the electron density.

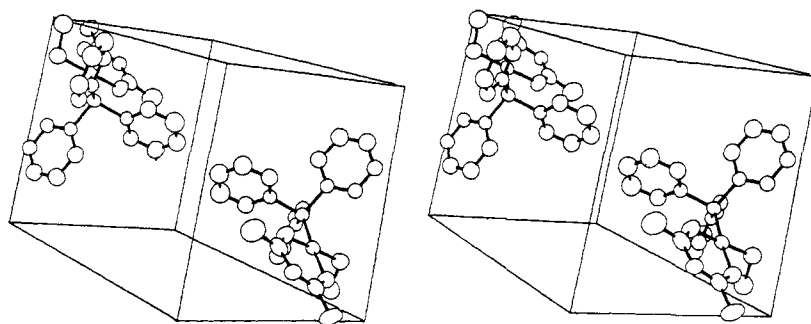


Figure 2. A stereo pair representation of the unit cell. The *a* axis extends from right to left, the *b* axis extends from top to bottom, and the *c* axis extends from back to front.

times the esd of the parameters. Of the 1437 reflections used in the refinement, there were 55 for which $||F_o| - |F_c||$ slightly exceeded $3\sigma(F_o^2)$. No dependence of the $\sum w(|F_o| - |F_c|)^2$ values on the indices, on $(\sin \theta)/\lambda$, or on $|F_o|$ was noted. The error in an observation of unit weight is 1.50.

A listing of observed and calculated structure factor amplitudes for those data included in refinement is given in Table I.¹⁴ The final positional and thermal parameters are listed in Tables II and III, with root-mean-square amplitudes of vibration given in Table IV.¹⁴

Table III. Positional and Thermal Parameters and Their Standard Deviations for Isotropically Refined Atoms^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
C(11)	0.111 (1)	-0.237 (1)	0.452 (1)	3.3 (3)
C(12)	0.217 (1)	-0.292 (1)	0.513 (1)	4.7 (3)
C(13)	0.337 (2)	-0.212 (2)	0.631 (1)	5.8 (3)
C(14)	0.348 (2)	-0.082 (2)	0.682 (1)	6.5 (4)
C(15)	0.245 (2)	-0.023 (1)	0.619 (1)	5.9 (4)
C(16)	0.125 (2)	-0.105 (1)	0.503 (1)	4.9 (3)
C(21)	-0.226 (1)	-0.391 (1)	0.336 (1)	3.6 (3)
C(22)	-0.233 (2)	-0.318 (1)	0.440 (1)	5.5 (3)
C(23)	-0.381 (2)	-0.361 (2)	0.452 (2)	7.6 (4)
C(24)	-0.511 (2)	-0.470 (2)	0.362 (1)	6.5 (4)
C(25)	-0.503 (2)	-0.539 (2)	0.263 (1)	6.3 (4)
C(26)	-0.358 (2)	-0.499 (1)	0.249 (1)	5.2 (3)
C(31)	-0.009 (1)	-0.481 (1)	0.249 (1)	3.7 (3)
C(32)	-0.032 (2)	-0.585 (1)	0.290 (1)	5.3 (3)
C(33)	-0.001 (2)	-0.706 (2)	0.240 (1)	5.9 (3)
C(34)	0.049 (2)	-0.715 (1)	0.152 (1)	5.7 (3)
C(35)	0.072 (1)	-0.614 (1)	0.113 (1)	4.5 (3)
C(36)	0.043 (1)	-0.494 (1)	0.160 (1)	4.1 (3)

^a Numbers in parentheses are estimated standard deviations in the last significant digit.

(14) See the paragraph concerning availability of supplementary material at the end of the paper.

Results

Crystal Structure. The structure of $\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_2\text{H}_5)(\text{PPh}_3)$ as it occurs in the crystal is shown in Figures 1 and 2. The bond distances and bond angles are listed in Tables V and VI. The structure has no surprising or unusual features. The coordination geometry of the nickel atom is square, the geometry about the phosphorus atom is tetrahedral, and the acetylacetonate moiety has dimensions very similar to those in numerous other $\text{C}_5\text{H}_7\text{O}_2\text{M}$ moieties. The entire structure closely resembles that of its methyltricyclohexylphosphine analog, $\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)(\text{CH}_3)[\text{P}(\text{C}_6\text{H}_{11})_3]$.²

The portion of this structure of greatest interest is the ethylnickel group. This appears as a perfectly normal

Table V. Bond Lengths (Å)

Ni-P	2.137 (4)	O(1)-C(3)	1.28 (1)
Ni-C(1)	1.97 (1)	O(2)-C(4)	1.30 (1)
Ni-O(1)	1.909 (9)	C(1)-C(2)	1.56 (1)
Ni-O(2)	1.913 (9)	C(3)-C(5)	1.56 (2)
P(1)-C(11)	1.80 (1)	C(3)-C(7)	1.36 (2)
P(1)-C(21)	1.83 (1)	C(4)-C(6)	1.53 (2)
P(1)-C(31)	1.82 (1)	C(4)-C(7)	1.40 (2)
C(11)-C(12)	1.39 (2)	C(21)-C(22)	1.42 (2)
C(11)-C(16)	1.38 (2)	C(21)-C(26)	1.39 (2)
C(12)-C(13)	1.45 (2)	C(22)-C(23)	1.46 (2)
C(13)-C(14)	1.37 (2)	C(23)-C(24)	1.40 (2)
C(14)-C(15)	1.42 (2)	C(24)-C(25)	1.35 (2)
C(15)-C(16)	1.44 (2)	C(25)-C(26)	1.43 (2)
C(31)-C(32)	1.41 (2)	C(31)-C(36)	1.40 (2)
C(32)-C(33)	1.45 (2)	C(32)-C(33)	1.45 (2)
C(33)-C(34)	1.38 (2)	C(33)-C(34)	1.38 (2)
C(34)-C(35)	1.36 (2)	C(34)-C(35)	1.36 (2)
C(35)-C(36)	1.41 (2)	C(35)-C(36)	1.41 (2)

Table VI. Bond Angles (deg)

P-Ni-O(1)	91.4 (3)	C(11)-P-C(31)	106.2 (6)
P-Ni-C(1)	89.1 (4)	C(21)-P-C(31)	102.6 (6)
O(1)-Ni-O(2)	92.5 (3)	Ni-O(1)-C(3)	126.8 (9)
O(2)-Ni-C(1)	86.9 (5)	Ni-O(2)-C(4)	125.6 (9)
P-Ni-O(2)	175.6 (3)	O(1)-C(3)-C(5)	126 (1)
O(1)-Ni-C(1)	179.3 (5)	O(1)-C(3)-C(7)	113 (1)
Ni-P-C(11)	116.9 (4)	C(5)-C(3)-C(7)	120 (1)
Ni-P-C(21)	111.5 (4)	O(2)-C(4)-C(6)	114 (1)
Ni-P-C(31)	114.4 (4)	O(2)-C(4)-C(7)	126 (1)
Ni-C(1)-C(2)	108.1 (9)	C(6)-C(4)-C(7)	120 (1)
C(11)-P-C(21)	103.8 (6)	C(3)-C(7)-C(4)	123 (1)
Angles within the Phenyl Rings at the Carbon Specified			
C(11)	120 (1)	C(21)	121 (1)
C(12)	119 (1)	C(22)	117 (1)
C(13)	120 (1)	C(23)	120 (2)
C(14)	121 (1)	C(24)	122 (2)
C(15)	118 (1)	C(25)	120 (1)
C(16)	121 (1)	C(26)	120 (1)
C(31)	120 (1)	C(31)	120 (1)
C(32)	119 (1)	C(32)	119 (1)
C(33)	118 (1)	C(33)	118 (1)
C(34)	123 (1)	C(34)	123 (1)
C(35)	121 (1)	C(35)	121 (1)
C(36)	119 (1)	C(36)	119 (1)

alkylmetal group in every respect. The Ni-C distance, 1.97 (1) Å, agrees well with other reported Ni-C(σ) dis-

tances,² the average of which is 1.95 Å. The C(1)–C(2) distance, 1.56 (1) Å, and Ni–C(1)–C(2) angle, 108.1 (9)°, are as expected for an ordinary Ni–CH₂–CH₃ group.

Nmr. A portion of the proton spectrum at room temperature in acetone-*d*₆ is shown in Figure 3; shown here are two singlets at τ 8.18 and 8.64 of relative intensity 3 assigned to the methyl groups of the acetylacetonato ligand and a signal of relative intensity 5 at τ 9.79 which must be due to the C₂H₅ protons. There is also a signal of relative intensity 1 at τ 4.75 which is due to the methyne proton of the acetylacetonato ligand as well as a large multiplet from the 15 phenyl protons. The entire spectrum is as summarized by Yamamoto, *et al.*,³ and agrees with the molecular structure found in the crystal in every respect, except that the five hydrogen atoms of the ethyl group appear as a sharp singlet, with a relative intensity of 5. Also, in agreement with Yamamoto, *et al.*,³ we find that in pyridine the methyl and methylene resonances of the ethyl group give rise to a complex multiplet. This can presumably be considered as a second-order spectrum owing to the similar magnitudes of the J_{H-H} and $\Delta\tau$ values.

In an attempt to see if the signal for the C₂H₅ group would broaden and split as it should if the nmr equivalence of the CH₂ and CH₃ protons were due to an exchange process, spectra were recorded at lower temperatures. These are shown in Figure 3. It will be seen that the signals for the acetylacetonato methyl groups become sharper between 28 and –4°. The reason for this will be discussed below. From –4 to –77° all of the signals broaden, but the C₂H₅ signal broadens a little more than those of the methyl groups. Broadening of all signals is due to increasing viscosity, while the somewhat greater broadening of the C₂H₅ signal is due to the fact that the difference in the chemical shifts for the CH₂ and CH₃ protons, which is accidentally zero at room temperature, increases slightly at lower temperatures. An increase of even a few cycles would give rise to pronounced broadening because of the resulting second-order spectrum (see the above remarks regarding the spectrum in pyridine). The explanation just proposed for the behavior of the C₂H₅ signal shown in Figure 3 of course begs the question of whether a dynamical process is involved. The only point we are trying to make here is that the observed results *can* be explained without postulating any site averaging process. That they *should* be so explained is proved by the ¹³C spectra which will be discussed presently.

Before turning to the ¹³C spectra, the temperature dependence of the widths of the acetylacetonato lines between 28 and –4°, as seen in Figure 3, will be further elucidated. As shown in Figure 4, on increasing the temperature these lines undergo a continued broadening, coalescence, and then sharpening of the single line in a manner clearly indicating a time averaging of their environments (which are, of course, different, as Figures 1 and 2 show). The coalescence temperature is $64 \pm 4^\circ$.

We have no proven explanation for this averaging, but three plausible mechanisms are: (1) dissociation and recombination of the phosphine ligand, (2) dissociation of one Ni–O bond, internal rotation in the temporarily unidentate acetylacetonato ligand followed by formation of a new Ni–O bond, and (3) coordina-



Figure 3. The proton nmr spectrum in the aliphatic proton region at various temperatures, solvent CD₃COCD₃. The small signal at the left is due to residual protium in the deuterioacetone.

tion of excess phosphine, present as an impurity, followed by elimination with reversal of the positions of the Ni–C₂H₅ and Ni–PPh₃ bonds. Each of these processes is known to occur in some other system. We have not attempted to elucidate this behavior further since it is not germane to our main objective.

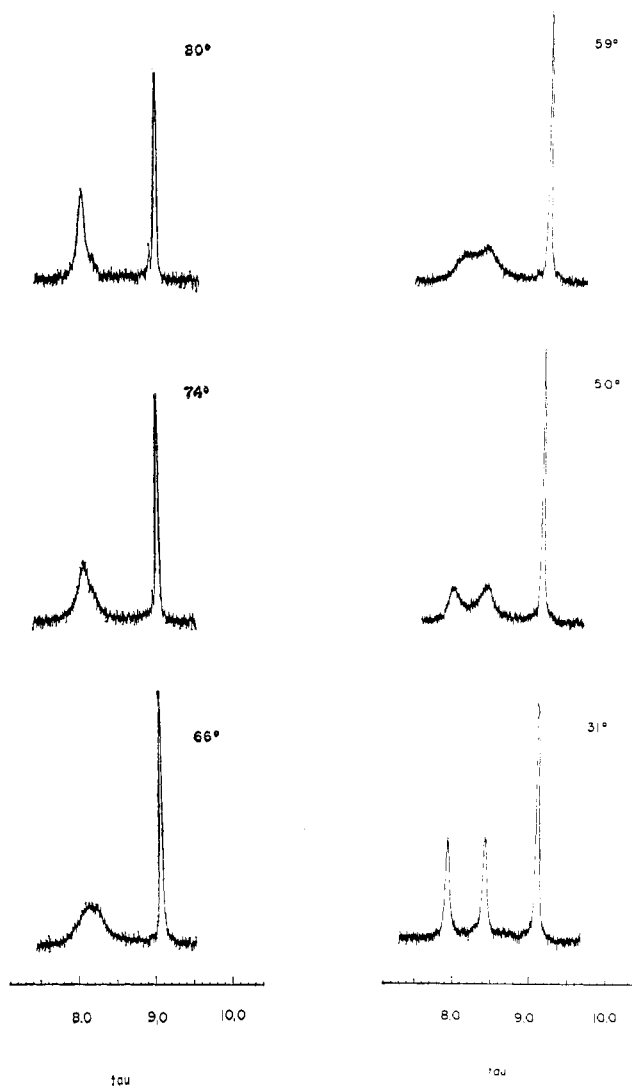


Figure 4. The proton nmr spectrum in the aliphatic proton region at elevated temperatures, solvent C_6D_6 . The sharp singlet is due to the C_2H_5 protons, while the pairs which collapse and coalesce are due to the acetylacetonato methyl groups.

The carbon-13 nmr spectra shown in Figure 5 constitute the most informative part of this study. Spectrum a shows the entire spectrum recorded in toluene- d_8 with broad-band proton decoupling. The assignment is straightforward. The signals at 27.4 and 26.8 are for the methyl carbon atoms, that at 99.9 is for the CH carbon atom, and that at 186.3 is for the carbonyl atoms of the acetylacetonato ligand. These assignments are in accord with those of a previous investigation of several metal acetylacetonates¹⁵ and are supported by the splitting observed when the protons are not decoupled. Thus the CO signal remains a singlet, the CH signal becomes a doublet, and the methyl signals become quartets. These splittings (for all but the CO carbon atoms) are shown in Figure 5b. Also seen in Figure 5a are signals for the phenyl groups, the phenyl and methyl carbon atoms of the toluene solvent, and the TMS. Finally, there are two lines at 6.8 and 13.9 ppm which must be assigned to the carbon atoms of the ethyl group.

(15) J. C. Hammel and J. A. S. Smith, *J. Chem. Soc. A*, 1855 (1970).

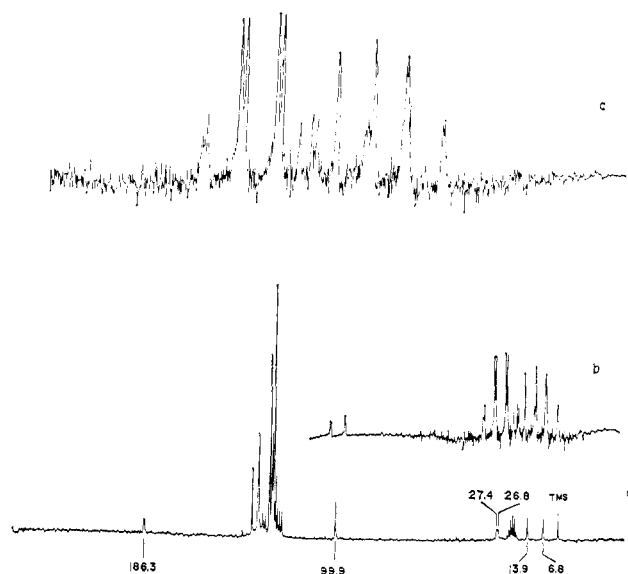


Figure 5. Carbon-13 nmr spectra at 25° of $(C_5H_7O_2)Ni(PPh_3)_2 \cdot C_2H_5$. Details of instrumental settings and procedures will be found in the Experimental Section. (a) In $C_6D_5CD_3$ with broad-band proton decoupling. The multiplet at ca. 20 ppm is due to the methyl carbon atom of the solvent. The signals at ca. 130 ppm are from the aromatic carbon atoms of both the solvent and the triphenylphosphine ligands. (b) In C_6D_6 without decoupling and omitting TMS. (c) An enlarged view of the high-field region.

The fact that the carbon atoms of the ethyl group give separate sharp signals shows that processes 1 and 2 are not occurring rapidly. By recording the ^{13}C spectrum without decoupling the protons, the assignment of the two lines at 6.8 and 13.9 ppm was conclusively confirmed and the absence of any proton scrambling process whatever was also demonstrated. In order to avoid interference by the toluene methyl group, the undecoupled spectrum was recorded on a solution in C_6D_6 . The portion of interest here is shown enlarged in Figure 5c.

Beginning at low field we see a 1:3:3:1 quartet of doublets. As already noted this is actually due to the two acetylacetonate methyl carbon atoms, each giving rise to a quartet ($J_{C-H} = 127.1$ Hz) and displaced by about 15 Hz. A second quartet begins between the highest and next highest members of the one just discussed. It has a main splitting of 125.4 Hz and shows no further fine structure. This corresponds to the line at 13.9 ppm in the decoupled spectrum and allows the conclusive assignment of that line to the methyl carbon atom of the ethyl group. Finally there is a 1:2:1 triplet with a main splitting of 132.1 Hz and a very slight (ca. 1 Hz) secondary splitting of each component into a doublet. This has its two lower field components partially overlapped by the two uppermost components of the $-CH_2CH_3$ quartet. Clearly, this triplet is due to the methylene carbon atom of the ethyl group. The slight splitting of each component is presumably due to weak coupling to the ^{31}P nucleus.

Discussion

The study reported here rules out entirely the suggestion of Yamamoto, *et al.*,³ that scrambling of the ethyl protons is occurring rapidly on the nmr time scale. It is clear from Figure 5c that three protons re-

main coupled to one carbon atom and two remain coupled to the other. Moreover, all the spectra in Figure 5 indicate that the α - and β -carbon atoms are nmr non-equivalent in toluene and benzene as well as in pyridine.

These results do not rule out the possibility that process 1 occurs, or even that it occurs rapidly, but, if it does, rotation of the olefin cannot be rapid. If process 1 occurred rapidly the ^{13}C spectrum would not necessarily be very different from that expected if it did not occur at all. If the instantaneous concentration of the olefin intermediate were small, the magnitudes of the ^1H - ^{13}C couplings would not be measurably affected. In any case the H- α -C couplings would be preserved. If spin correlation were preserved in the transfer of a β -H from the carbon atom to the nickel atom, which is entirely possible, the methyl ^{13}C quartet would also be preserved essentially unchanged. Thus, we cannot rule out the occurrence of process 1 but we can say with certainty that *if it occurs* it is not followed by rapid rotation of the olefin.

The nmr equivalence of the methyl and methylene hydrogen atoms at 100 MHz is apparently due to accidental equivalence of their chemical shift values under the conditions of measurement. Their separa-

tion in the solvent pyridine may be due to coordination of the pyridine to the nickel atom, thereby altering its electronic structure and, in turn, the relative chemical shifts of the methyl and methylene protons. It is also possible that the polar nature and diamagnetic anisotropy of the pyridine molecule cause it to associate with molecules of **1** in such a way as to shift the two sets of protons differently, quite apart from any specific donor interaction toward the nickel atom.

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Supplementary Material Available. A listing of structure factor amplitudes (Table I) and root-mean-square amplitudes of vibration (Table IV) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 \times 148 mm, 24 \times reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-4820.

Simulation and Evaluation of Chemical Synthesis. Computer Representation and Manipulation of Stereochemistry^{1a}

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Abstract: An ordered-list representation of double bond and asymmetric carbon atom stereochemistry is described which facilitates machine manipulation and analysis. Procedures have been developed and implemented to transform a three-dimensional structure or a two-dimensional structural diagram having wedged and hashed bonds into the ordered-list connection table, and to transform an ordered-list connection table into a stereochemically unambiguous structural diagram. Stereochemical requirements and selection rules of reactions, or their inverse, transforms, are represented in *ALCHEM*, a machine readable English-like language. Algorithms are outlined for manipulating the ordered-list connection table of a target structure according to the selection rules of a given transform, producing all stereochemically correct synthetic precursors of that target. From these results many types of problems involving stereochemistry are now amenable to computer analysis. The described algorithms have been utilized in a computer program for the design of organic syntheses.

The first work in applying computers to the problem of planning an organic synthesis² considered molecules in a topological sense, devoid of any shape or spatial arrangement. Although the structural diagram entered by the chemist, and produced as output by the program, appeared to carry three-dimensional information, this information was ignored by the program. In many synthetic targets, *e.g.*, prostaglandins, stereochemistry is the primary feature to be controlled. Further, the

spatial arrangement of groups in a target can provide powerful heuristics to help select the applicable synthetic procedures for constructing that spatial arrangement. Many chemical reactions occur according to known stereochemical selection rules, *e.g.*, Woodward-Hoffmann rules; a complete representation of chemistry should embody these principles. This paper describes techniques for machine representation and analysis of stereochemistry. While we are concerned here with incorporation of stereochemistry in a computer program for the design of organic syntheses (specifically the Simulation and Evaluation of Chemical Synthesis (SECS) program), these results are equally applicable to any computer approach which deals with chemical structures and changes in chemical structure.

(1) (a) Presented in part at the Symposium on Stereochemistry, 164th National Meeting of the American Chemical Society, New York, N. Y., Sept 1972; (b) NSF Trainee, 1969-1971.

(2) E. J. Corey and W. T. Wipke, *Science*, **166**, 178 (1969); E. J. Corey, W. T. Wipke, R. D. Cramer III, and W. J. Howe, *J. Amer. Chem. Soc.*, **94**, 421, 431 (1972); E. J. Corey, R. D. Cramer III, and W. J. Howe, *ibid.*, **94**, 440 (1972).